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Characterization of Various Materials Using Refractometry

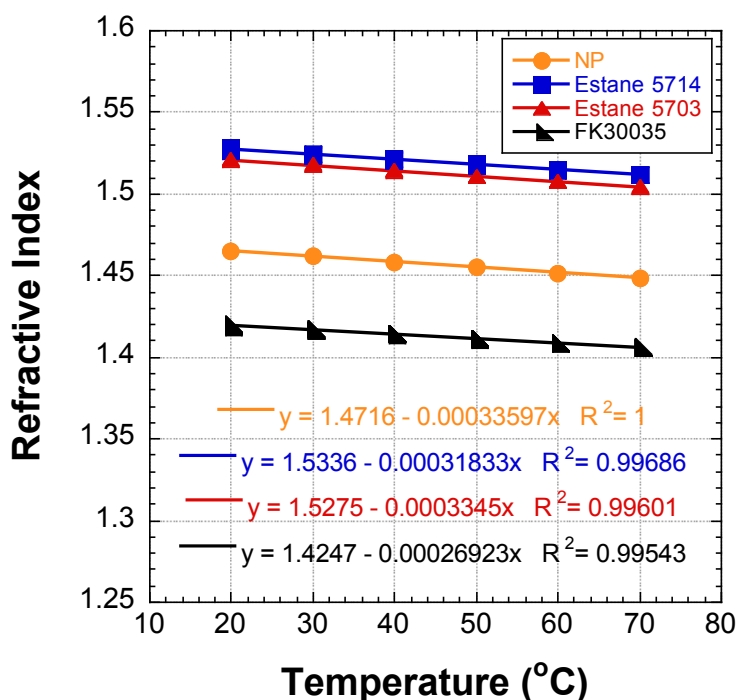
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Abstract:

Refractive index (RI) is a fundamental physical property of a material. However, the RI values of several binders, including nitroplasticizer (NP), Estanes, and Kelf/FK 800, are not available in literature. Further, their temperature dependencies are undocumented either. In this study, we have developed a set of methodologies to accurately and effectively determine the RIs of these binder materials between 20 and 70°C. The RIs of these binders without aging show linear correlations with temperature, as shown in the figure below. Among these materials, Estane 5714 has the highest RI whereas FK800 has the lowest RI. As materials age, the changes in their RIs are different, suggesting different aging behavior of these binders upon heating. Typically, NP and Estane degraded through hydrolysis give lower RIs than the baseline materials. However, when Kelf/FK800 materials thermally age, their RIs increase. Overall, this study demonstrates refractometry is a sensitive technique to detect aging signs in various materials of interest.



1. Introduction

Refractive index (RI) is a measure of how light propagates through a material in comparison to propagation through a vacuum. A medium with a high RI value is highly polarizable, and light passes through it slowly. Automatic refractometers are often used in food and pharmaceutical industries, where the RIs are used to test products for quality assurance. However, few of these types of refractometers have been utilized for polymeric materials, even less so on how their RIs

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change with temperature. In this study, we have developed a set of methodologies using automatic refractometer to accurately and effectively measure liquid and solid materials. The materials studied are nitroplasticizer (NP), Estane, and Kelf/FK800 polymers, which are important binder materials used in LANL weapon applications. However, RI, a fundamental physical property, is not available in literature for these materials. This is especially true for the dependences of their RIs on temperature. This study fills this gap.

It is well known that the change in RI reflects changes in the properties of a material. This information can be used to characterize the aging behavior of the material. Since each material has a unique RI, for a polymer, RI is commonly used to determine its molecular weight, which is an essential property of its mechanical strength in many applications¹. Previous studies measure the RI value of polymers using Abbe refractometers or traditional hand-held refractometers by dissolving the polymer in a liquid. While these methods do work, the process is slow and requires several complicated calculations. Furthermore, most previous research has not measured the RI values of these polymers at the temperatures above ambient. In this work, simpler and more efficient methods were developed to accurately determine the RI values of polymer films at different temperatures.

2. Experimental

2.1. Instrumentation and Materials

In this study, an automatic J357 refractometer by Rudolph Research Analytical with optical wavelength of 589.3 nm was used to measure the RI values of various liquids and polymers with an optimal temperature ramping method. Due to the nature of these materials, the accuracy of their RI measurement is less than others, especially at high temperatures. To ensure the accuracy and time-efficiency, we used water to develop a temperature ramping method because the RIs of water at different temperatures can be found in literature. We optimized the procedures to measure the RIs of liquid and solid samples at various temperatures. Six liquid samples were: nitroplasticizer (NP) aged at 38, 55, and 70°C. Half of the NP samples were aged with 50% VCE (vinyl copolymer elastomer)/filler composite and the other half aged with 100% VCE polymer for two years. Another of significant element of the PBX 9501 binder measured was Estane[®] 5703 and Estane[®] 5714; both block copolymers of poly(ester urethane) and poly(ether urethane), respectively. The Estane 5703 samples included pristine, aged, and NP soaked Estane. These polymers were stored in pellet form and heat pressed into film form to ensure a smooth surface. Pristine films were soaked in NP at room temperature to obtain the NP soaked samples used Estane 5703 and 5714 were soaked in NP at room temperature until they were saturated with NP. Several Kelf/FK 800 samples were also tested. These polymer films were prepared similarly to the Estane film. In addition to the pristine samples, eight samples were aged in an oven at 45°C for 14 months prior to the measurement.

2.2 Refractometer Calibration

To calibrate the refractometer, water and α -Bromonaphthalene were used². Since the materials tested have RIs ranging from 1.45 to 1.55, we determined the best calibration would need a liquid above and one below this range. To ensure consistency for all measurements, the refractometer was calibrated before the first run, and then validated with water after each sample

was cleaned off. If the refractometer did not pass the validation, it would be recalibrated. The detail calibration procedures are given in Appendix A.

3. Results and Discussion

3.1. Method Development for Liquid Samples

3.1.1. RI of Water

Since the RI of water can be found from literature³, we used water to develop a method for the RI measurements of liquid at different temperatures. To do so, three methods, as listed in Table 1, were explored. The ultimate goal was to obtain the most accurate results with effective instrument time without risking evaporation of fluid. While all three have minimal percent error, we conclude Method 3 is optimal: waiting for temperature to stabilize ± 0.02 for 20 seconds and for RI measurement ± 0.00004 for 30 seconds, respectively.

Table 1. Summary of the methods used for measuring RIs of water between 20 and 70°C. The RIs of water from literature are used to evaluate the accuracy of each method.

Method No.	Control	Temperature (°C)	Refractive Index	Literature Value	Percent Error (%)	Average Error
1	± 0.02 °C for 15sec No measurement control	20.00	1.33299	1.33299	0.00000	.00440%
		30.00	1.33186	1.33192	0.00450	
		40.01	1.33053	1.33051	0.00150	
		50.03	1.32898	1.32891	0.00527	
		60.04	1.32722	1.32718	0.00301	
		70.03	1.32527	1.32511	0.01210	
2	± 0.02 °C for 30sec ± 0.00002 RI for 60sec	20.00	1.33299	1.33299	0.00000	.00188%
		30.00	1.33190	1.33192	0.00150	
		40.00	1.33054	1.33051	0.00225	
		50.00	1.32896	1.32891	0.00376	
		60.00	1.32715	1.32718	0.00226	
		70.00	1.32513	1.32511	0.00151	
3	± 0.02 °C for 20sec ± 0.00004 RI for 30sec	20.00	1.33299	1.33299	0.00000	.00226%
		30.00	1.33191	1.33192	0.00075	
		40.00	1.33055	1.33051	0.00300	
		50.00	1.32898	1.32891	0.00526	
		60.00	1.32718	1.32718	0.00000	
		70.00	1.32517	1.32511	0.00453	

3.1.2. RI of NP Samples

From the above work, we decided to use Method 3 for the RI measurement of the NP samples. Figure 1 presents a set of NP samples – baseline and aged NP samples. The RI of NP linearly decreases with increasing temperature with a correlation of $RI(T) = 1.4716 - 0.00033597 \cdot T$ (°C) between 0 and 70°C. The RI at 20°C is 1.462, which is consistent with literature value (1.462 - 1.464)⁴.

Compared to the baseline NP, the samples aged at 38°C and 55°C for two years show a slight increase; whether it was aged together with 50% VCE or 100% VCE did not change the result.

Their RIs all linearly decrease as the temperature increases. The results suggest that aging at 38°C and 55°C does not change the NP properties significantly.

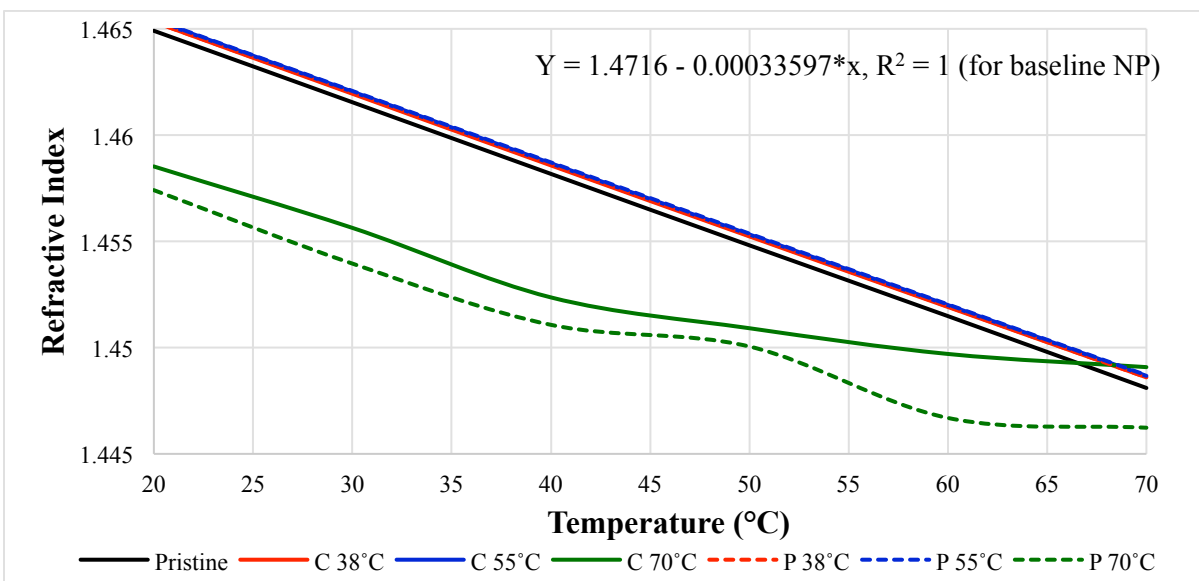


Figure 1: RIs of baseline and aged NPs at different temperatures for 2 years. “C” stands for NP aged together with 50% VCE/filler composite, while “P” stands for NP aged together with 100% VCE polymer. Method 1 was used to measure the 70°C samples, and Method 3 was used to measure the rest of samples.

On the other hand, in the case of the 70°C aged samples, the overall RIs are noticeably lower than the other samples, indicating the 70°C samples are less polarizable than the baseline sample, and probably has lower molecular weight molecules. Unlike the other samples, the RIs of the 70°C samples change nonlinearly with increasing temperature. It is especially true when the measurement temperatures were above 40°C, suggesting that some volatile compounds start to evaporate at elevated temperatures. This phenomenon was not observed for the samples aged at 38 or 55°C. Clearly, the 70°C samples were greatly degraded during the aging process.

It is worth more discussion on the nonlinearity between the RI and temperature for the 70°C samples. It is suspected that some compounds start to evaporate at high temperatures, which changes its RI. To ensure accurate measurements, we compared the RI measurements of the 70°C samples using Methods 1 versus 3. When we developed a method for liquid samples, we concluded that Method 3 is the optimal one, and used this method to measure the RIs for most of NP samples. However, when using Method 3 to measure the 70°C samples, we found greatly increased RIs at the temperatures above 40°C, as shown in Figures 2a and 2b. The large changes in RI could be due to evaporation of low boiling point compounds, since Method 3 does take longer time to finish than Method 1. Therefore, for the samples containing volatile compounds, Method 1 is more suitable, as the liquid has less time to vaporize. The results of the 70°C samples in Figure 1 were measured using Method 1.

As for the volatile compounds in the 70°C samples, they are suspected to be nitric acid or similar acidic compounds⁵. The RI of nitric acid is 1.397 at 16.5°C. The presence of these kinds of

acidic compounds in the aged samples decreases their RIs. As expected, when these volatile compounds leave the samples during the temperature ramping process, the RI of the residual sample increases.

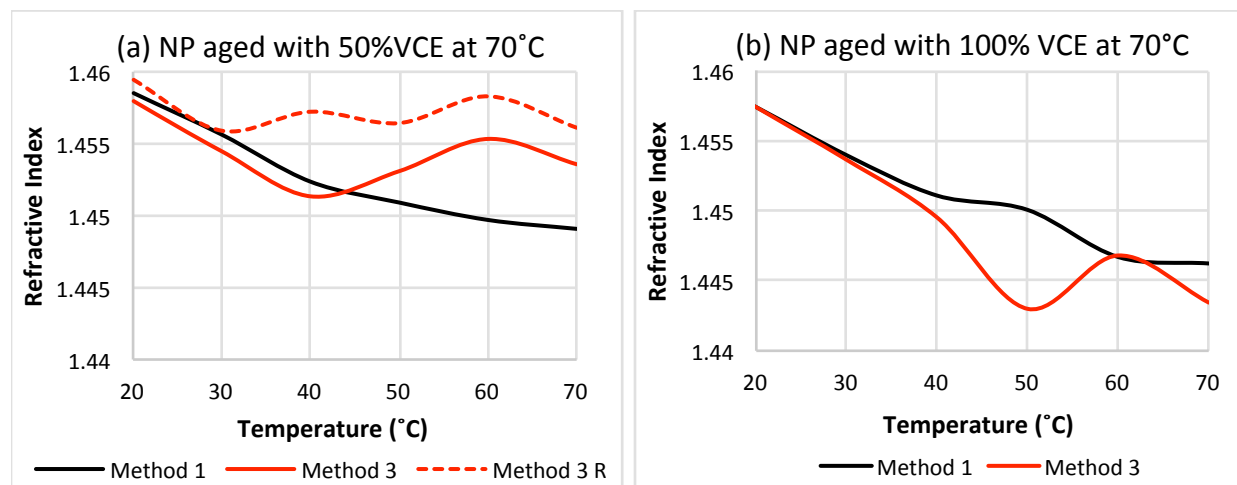


Figure 2. Effect of different measuring methods on the RIs of the NP aged together with 50% VCE at 70°C (a) and of the NP aged together 100% VCE at 70°C (b) between 20°C and 70°C.

3.2. Method Development for Solid Samples

Measuring the RI of solid samples proved more difficult than liquids, since the automatic refractometer requires good contact with the prism. Thus, there are limitations on types of solids to be measured directly. While rigid solids can be measured, another liquid with a higher RI than the solid must also be present. For direct measurement, the solid must have a smooth surface and flexible or soft such that it can be compressed easily. The solid should be clear enough so that some light can pass through. Fortunately, once Estane pellets were pressed into the thin films (~1mm thickness), the film samples match these requirements. Depending on the type of samples, different methods, as summarized in Table 2, were implemented.

Table 2: Summary of the methods used for measuring RIs of solid samples between 20°C and 70°C.

Method No.	Temperature Control	Measurement Control
1	± 0.03 30 sec	$\pm .00002$ 60 sec
2	± 0.02 45 sec	N/A
3	± 0.02 40 sec	$\pm .00004$ 30 sec
4	± 0.02 20 sec	$\pm .00004$ 60 sec

3.2.1. RI of Pristine Estane 5703 and Estane 5714 Films

For all pristine samples of Estane 5703, Method 1 in Table 2 was used. Compared with liquids, the temperature takes longer time to obtain stable RIs within $\pm .00002$. Therefore, 60 seconds was used to ensure the accurate measurement. Since both Estane samples melt at temperatures higher than 70°C, the temperature ramp stops at 70°C. Furthermore, since Estane 5703 started to melt near 60-70°C, redoing the measurements using the same sample noticeably changed the RI

of the polymer. Interestingly, each redo sample gives a better linearity with temperature than the sample being measured at the first time, as shown in Figure 3a presents the RIs of two Estane samples, collected at different regions of the film. The results are slightly different, which suggests heterogeneity in the Estane 5703 sample.

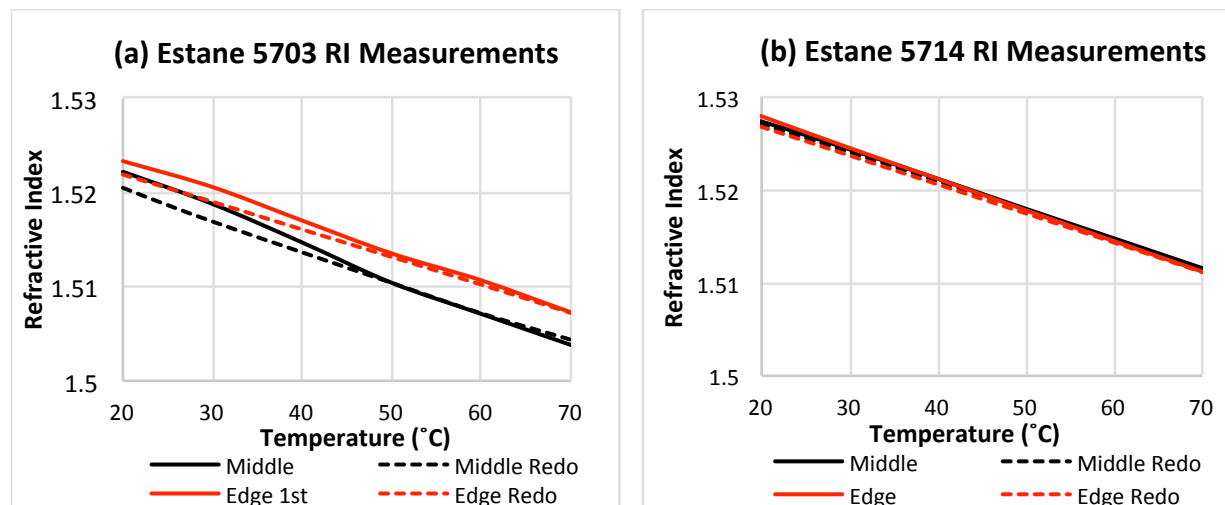


Figure 3. RIs of pristine Estane 5703 (a) and pristine Estane 5714 (b) between 20°C and 70°C.

As seen in Figure 3b, the RI values of the edge and middle pieces from Estane 5714 film show little difference. The redo for each sample is almost identical to the 1st measurement of the sample. Because the 5714 samples were clearer than the 5703 samples, we suspect the 5714 measurements are more precise.

Compared to Estane 5703, Estane 5714 is stiffer and more rigid, thus getting an accurate reading proved difficult. Method 1 in Table 2 was used for this polymer mainly to be consistent with Estane 5703, as both are our baseline samples. After we measured each sample, the refractometer was recalibrated to ensure consistent results. In Figure 4, Estane 5714 consistently has a higher RI than 5703, but the similar slopes (0.00031833 verses 0.0003345) of both lines indicate the dependences of their RIs on the temperature are similar to each other, although Estane 5714 did not melt as much as Estane 5703 when heated to 70°C. Typically, a higher RI usually indicates a polymer with higher molecular weight compared to the similar polymers with a lower RI¹. Indeed, based on the gel permeation chromatography of these two materials, the molecular weight of Estane 5714 is ~178 kDa while the molecular weight of Estane 5703 is ~125 kDa. The results from these two measurements agree well. This result demonstrates that the RI measurement is a sensitive technique to detect different properties of polymer samples.

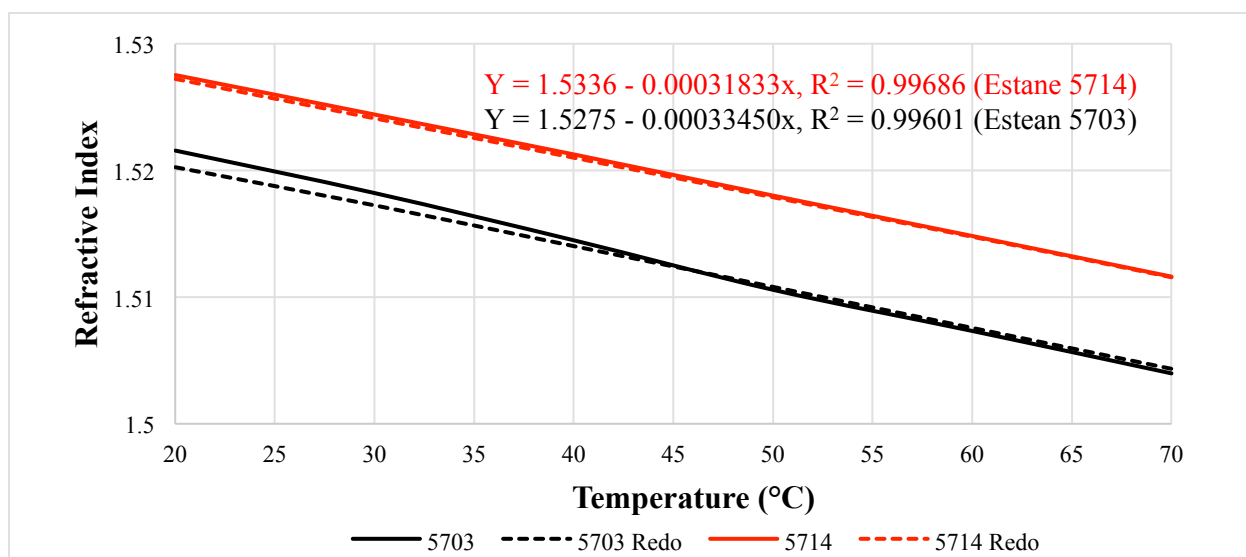


Figure 4: The RIs of Estane 5714 and 5703 samples between 20 and 70°C.

3.2.2. RI of Aged Estane 5703 Films

Estane 5703 naturally ages when exposed to temperature and moisture⁶. To investigate how the RI changes with polymer aging, we analyzed two old-aged Estane 5703 films, which were naturally aged for more than 10 years. Since the aged materials are cloudier and more brittle than the pristine Estane, it was difficult to get stable and accurate measurements. Since the RI reading took a long time to stabilize, we decided to use Method 2 in Table 2 for the RI measurement. The results of aged Estane samples are shown in Figure 5.

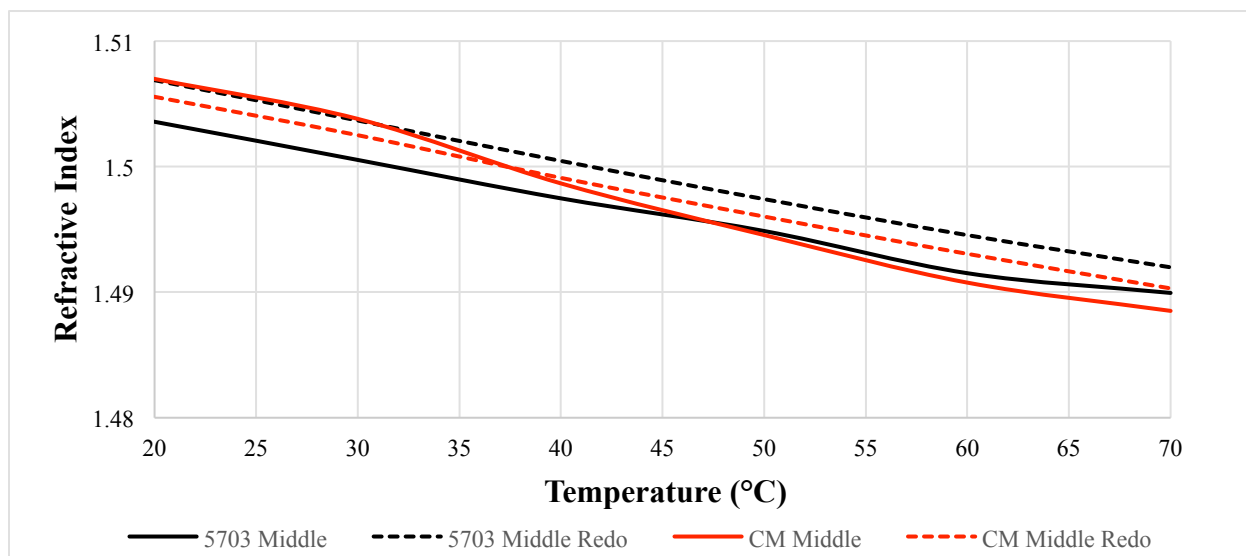


Figure 5: The RIs of two aged Estane 5703 samples between 20 and 70°C (Method 2 in Table 2 was used).

It is worth noting that the aged samples began to melt near 40°C, which is ~30°C lower than any of the pristine samples. After the samples were heated up to 70°C, the results from the second measurements were often different from the first measurement. Unlike the pristine samples, most of the aged samples had nonlinear temperature dependence. The results suggest that the

aged Estane 5703 samples are more thermally sensitivity than the pristine samples. The earlier work reported that when the hydrolysis occurs in the Estane 5703 materials, small molecules with $-OOH$ and $-OH$ functional groups formed⁶, the nonlinear behaviors of the RI vs. temperature (solid lines in Figures 5 and 6) for the aged Estane samples might be due to the evaporation of these alcohol and acidic molecules. As the first measurement drives the volatilizable molecules out of the samples, the RIs of the second measurement (dashed lines) become linear functions of temperature.

Figure 6 compares the RIs of Estane 5703 before and after hydrolytic aging. After hydrolysis, the RI of Estane 5703 decreases from ~ 1.522 to 1.505 at $20^{\circ}C$. The decreased RIs suggest the depolymerization and changed optical properties. This result also demonstrates the RI measurement as a sensitive technique to detect aging signs in polymer samples.

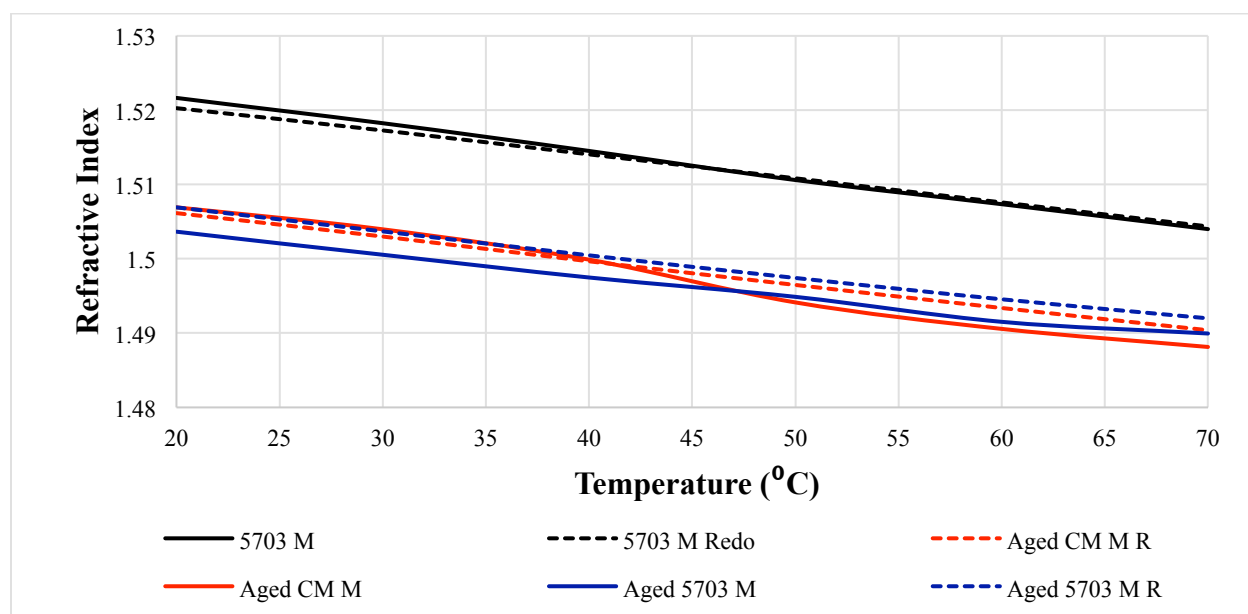


Figure 6: Comparison between Aged 5703 samples to Pristine 5703. M stands for middle of the film, and R stands for Redo of the exact same sample measured before.

Currently, we are conducting a set of aging experiments for Estane 5703 samples. During the aging process, their RIs will be measured. As more data are available, we hope to construct correlations between their molecular weights and RIs. These correlations should be useful for theoretical model development to predict the lifetime of Estane 5703 at different aging conditions.

3.2.3. RI of NP Treated Estane 5703 and Estane 5714

In some applications, Estane is used with NP to improve its adhesion properties. To study the effect of the interaction between NP and Estane polymer, we also examined Estane samples pre-treated with NP. When measuring the RI, Method 4 from Table 2 was used to quicken measurements so to minimize the NP vaporization. Figure 7 compares the RI results of NP soaked samples. Overall, these samples had lower RIs than their respective pristine polymers

(RI=1.522 at 20°C), but higher RIs than NP itself (RI = 1.465 at 20°C). Similar to pristine samples, the RI results from two measurements are almost identical, suggesting that the NP treatment does not change chemical properties of the Estane, and the evaporation of NP below 70°C was insignificant. Compared to Estane 5703 samples (86-2b and 93-1c), Estane 5714 (136-1) sample absorbs less NP despite identical NP soaking time. The smaller NP uptake in Estane 5714 results in smaller change in the NP treated sample.

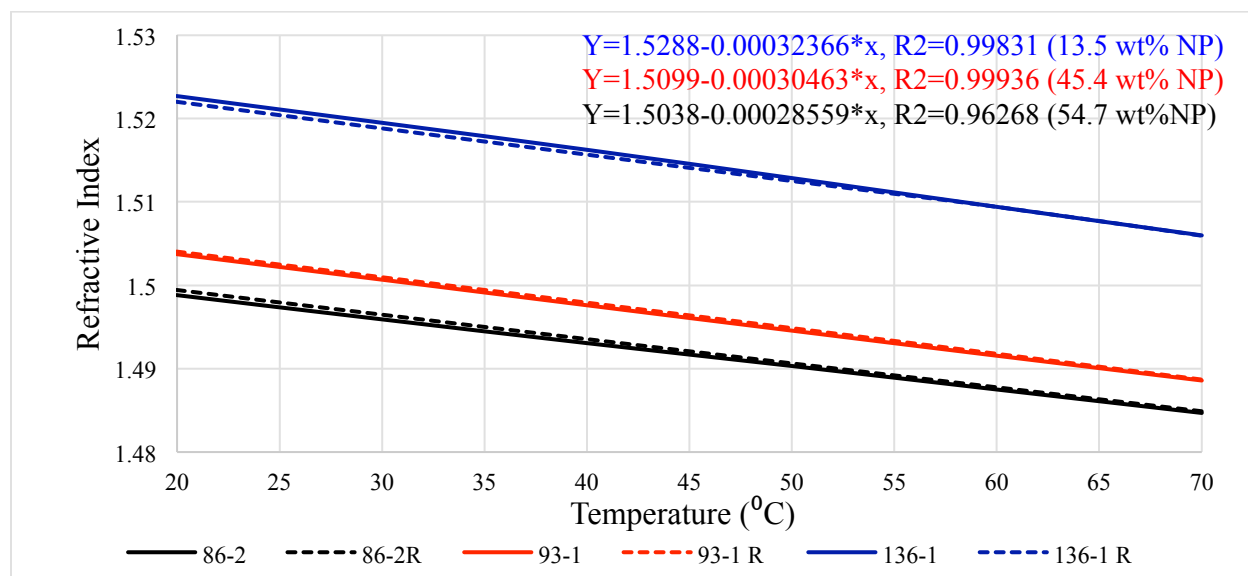


Figure 7: Effect of NP treatment on the RI of Estane samples. Sample 136-1 was made from Estane 5714 while Samples 86-2b and 93-1c were made from Estane 5703.

Consistently, the NP uptake in Estane 5703 directly affects the RIs of the NP treated samples. When the sample absorbs NP, its RI becomes lower compared to the pristine sample. Furthermore, when the NP uptake in Estane 5703 increases from 45.5 wt% to 54.7 wt%, its IR decreases from 1.5099 to 1.5038 at 20°C, and this trend is consistent through the temperature regime.

To better illustrate the effect of the NP treatment on the RIs of the Estane samples, Figure 8 presents the RIs of Estane 5714 (left) and 5703 (right) before and after the NP treatment. Clearly, the NP treatment has a larger effect on the RI of Estane 5703 than that of Estane 5714, which suggests the stronger interaction of NP with Estane 5703 than that with Estane 5714. The stronger interaction results in the solubility of NP in Estane 5703 as much as >1.2 g of NP/1 g of Estane 5703 whereas the solubility of NP in Estane 5714 is less than <0.16 g of NP/1 g of Estane 5714.

Compared to their pristine samples, all NP treated samples were more flexible and gel-like, indicating that NP plasticizes Estane and increases its strain but decreases its tensile strength. As expected, the more the sample absorbs NP, the softer the polymer becomes.

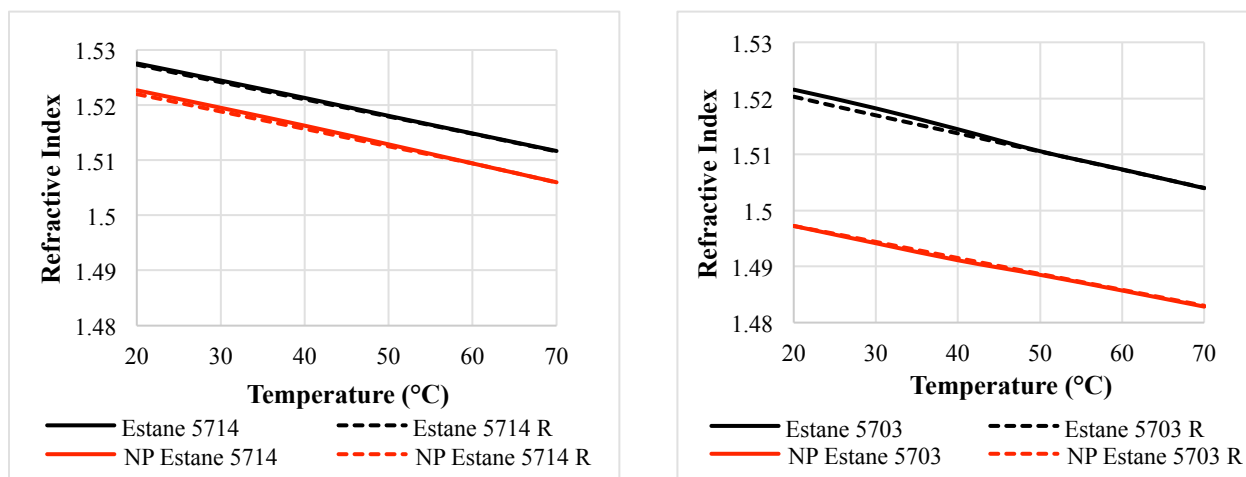


Figure 8. RIs of Estane 5714 (left) and 5703 (right) before and after NP treatment.

3.2.4 RI of Kel-F and FK Polymers

Another type of polymer measured was block copolymers of poly(chlorotrifluoroethylene vinylidene fluoride) (PCTFE and PVDF, respectively). For LANL weapon applications, depending on production years, they are referred to as KelF800 (made before 2000) and FK800 (made after 2002)⁷. The information of eight powdered samples is given in Table 3. The new production powders (FK800) were obtained from M-7 group, and KelF-646 was obtained from Pantex. These powders were thermally pressed into thin films (~1 mm thickness). After being pressed into the thin films, the eight films had been thermally annealed inside 45°C ovens for 14 months prior to the RI measurement. The pristine powder (FK800 Lot 30035 - referred as to FK lot 35) was pressed at the same procedures, and the film was used to provide a baseline for RI measurement.

Table 3. Summary of aging conditions of KelF/FK800 samples.

Sample No.	Polymer powder	Polymer powder	Aging conditions for polymer films
1	KelF 646	Made more than 20 years ago	Eight samples have been thermally aged inside 45°C ovens for 14 months before the measurement
2	FK Lot 8	New production	
3	FK Lot 9	New production	
4	FK Lot 20	New production	
5	FK Lot 29	New production	
6	FK Lot 30	New production	
7	FK Lot 35	New production	
8	FK Lot 35	Aged at 70°C air for two years	w/o aging
Pristine	FK Lot 35	New production	

However, because of lack of flexibility in the material at the temperatures below 40°C, getting an accurate RI measurement proved to be difficult. Instead of using a fluid as the instrument manual suggests², we manually measured their RIs at 20°C and 30°C and then used Method 4 to automatically measure the RIs between 40°C and 70°C. This revision of Method 4 was implemented for all fluoride samples to ensure the consistency between measurements. The

results of pristine samples are presented in Figure 9. For the pristine samples, various parts collected from the different regions of the film were measured to determine variability of the measurements. The results show more variation (± 0.00008) among samples at low temperatures than that at higher temperatures. We suspect that samples have slightly different RIs at low temperatures, but this difference gradually diminishes as the samples are thermally treated at the temperatures above 40°C. Overall, the RIs of these pristine samples show linear corrections with temperature. Based on the average values of these samples, the linear correlation of the RI against temperature is given in Figure 9 for the FK30035 polymer between 20 and 70°C.

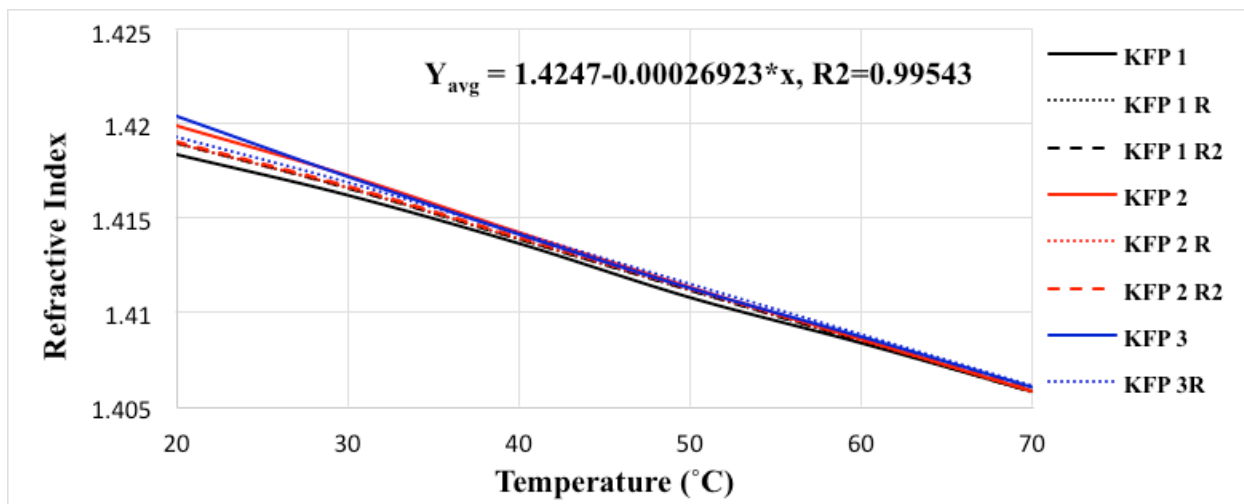


Figure 9: The RI values of pristine FK30035 film. KFP stands for FK35 Polymer, “R” stands for Redo on same sample, and “R2” stands for Redo on the same sample for the second time.

As shown in Figure 10, all of the aged samples give higher RI values than the pristine sample over the temperature range from 20 to 70°C. Since there are some variations in the production conditions over the years, it is hard to compare the RIs among all samples. However, the data for three samples made from FK Lot35 are comparable. These three samples are the pristine, No. 7 and No. 8 films. Compared to the pristine sample, both No.7 and No. 8 samples give higher RIs. Typically, the higher the RI is, the more polymerized or cross-linked the polymer is. Considering the chemical resistance of the FK800 polymer, chemical degradation occurring in these aged samples is unlikely. The increased RIs for the aged FK35 samples are most likely due to increased crystallinity during the low temperature aging process at 45°C. However, the difference between RIs of No. 7 and No. 8 is not significant, which confirms that the chemical stability of FK polymer does not change significantly after the powder was aged at 70°C for two years.

It is worth noting that in the RI measurements, the pristine film was more malleable as the temperature increases. However, for the aged samples, their physical rigidity was preserved better than the pristine samples after being heated up. This could indicate that the aged samples are thermally more stable than the pristine sample, which also suggests the increased crystallinity in the aged samples. Other characterization techniques will be conducted to verify this speculation.

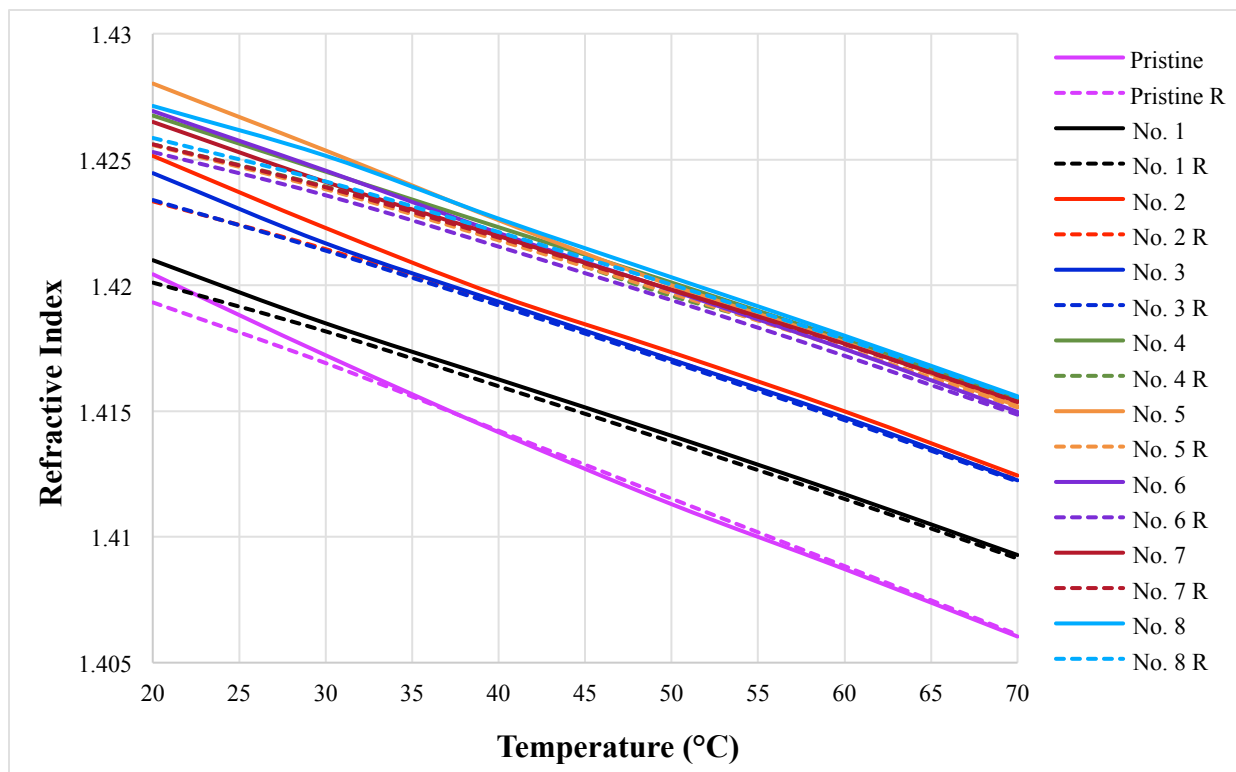


Figure 10. RIs of pristine and aged KelF/FK800 samples. “R” stands for Redo for the same sample originally measured.

4. Conclusion

In this study, we developed several methodologies to accurately and effectively measure the RIs of various binder materials over a wide temperature range. The RIs of several important binder materials, which are not available in literature, are determined. The RI results for these materials are summarized in Figure 11. The RIs of these binders are linear functions of temperature.

With developed methods, the RIs values of NP and aged NPs are determined between 20 and 70°C. When NP is aged at the temperatures below 55°C for two years, the RI changes only slightly, indicating the chemical composition did not change significantly. However, the NP samples aged at 70°C for two years had drastically decreased RI compared with the baseline and other aged samples, confirming the significant effect of high temperatures on the NP degradation⁵.

In addition to the pristine Estane samples, we also measured the RIs of NP treated Estane, hydrolyzed Estane, and thermally annealed KelF/FK. The results reveal different interactions between NP-Estane 5703 and NP-Estane 5714. The RI of hydrolyzed Estane 5703 is smaller than that of pristine Estane 5703. In contrast, the thermal annealing increases the RI of KelF/FK polymer, suggesting increased crystallinity in thermally aged KelF/FK polymers.

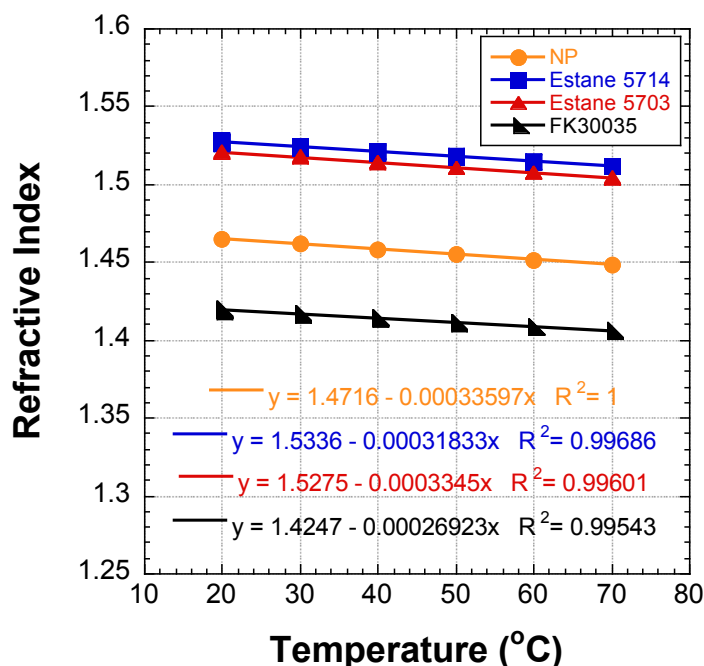


Figure 11. Summary of RIs of several binders used in LANL weapon applications.

Overall, this study demonstrates that automatic refractometers can be used to directly determine the RI values for solids without the supplement of dissolving the solid or using a base liquid, which greatly simplifies the RI measurement for the polymer samples and improves the reproducibility of the measurements. With this improved confidence, the changes in RI can be used as an effective indicator for the changing properties of materials.

5. Acknowledgements

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Appendix A. Operational Procedures

A.1. Calibration

1. Press menu and enter the password: 123
2. Click on “calibration” → “adjustment”
3. On the scrollbar, there will be different options for calibration. To use a pre-built method, scroll down to the method named “bromo” and wait for the prism to heat up.
4. After cleaning the prism, follow the instructions that the method gives.
5. Note: after placing water on the prism, the temperature will change. Wait for the temperature to adjust before moving on. Do not forget to dry the prism after wiping away the water because residual droplets will affect the α -Bromonaphthalene part.

To add/edit a new calibration method:

1. “menu” (password 123) → “add/edit methods” → “adjustment methods” → “add” → “copy from existing method”
2. Rename the method and it will return to the screen with all the methods. Click on method one wants to edit and enter the password 519
3. To change the fluid RI value you want to calibrate with, click on “fluid calibration values”
4. To change the temperature, click on “temperature”
5. Note: solid calibration is unnecessary, using liquids is enough for this instrument.

A.2. Validation instrument using water:

1. Click on “Zero” and choose “air” first. Make sure the prism is clean.
2. Choose “water” with the temperature at 20°C.

A.3. Changing and Adding Methods

1. To edit a method, first press the menu button on the homepage. If prompted with a password, type in 123.
2. Click on “add/edit methods” → “test methods”.
3. To make a new method, click on “Add” button → “copy from existing method” button. “Copying the standard method” is the easiest, and will require you to do less changes. Rename the method however you like. Afterwards, the screen will go back to the methods page. Scroll down to the bottom, click on the method and press edit
4. To edit a method, scroll through the methods until find the one you want to edit, highlight it, and click the edit button.
5. It is recommended not changing display configuration or style, as the standard one makes sense. To change temperature, press the temperature button and click on custom temperature. Do not use temperature correction.
6. “Measurement controls” adjusts how long it takes for the refractometer to record the sample’s RI by changing the ranges of the temperature or RI will stabilize to and for how long. Not to have RI control, unclick the box on the line under the temperature control.

7. To activate temperature ramping, click on “number of measurements” → “temp ramp”, you can decide on how many measurements and what temperatures to measure on the same page.

A.4. Measure Solid Samples

1. To measure solid sample, the solid kit attachment is needed.
2. First cut sample using the hole-punch that comes with the kit. It is designed to make the sample a little smaller than the size of the prism.
3. After cleaning the prism with acetone and calibrating the refractometer, place the sample on the prism, making sure that the solid has good contact with the prism.
4. Slide the solids kit onto the metal part of the refractometer until the white knob is right over the sample.
5. Twist the screw to lower the knob until it is pressing onto the sample. Look at the smart index on the refractometer's homepage; keep lowering the knob until smart index can read the measurement well or it is physically impossible to twist the knob anymore.

A.5. Current Methods besides Standard Methods on our Automatic Refractometer

“Solid Temp Ramp”: starts at 20°C ends at 70°C, records measurements every 10°C, stabilizes temperature to $\pm 0.02^\circ\text{C}$ for 20 sec, waits for measurement to stabilize $\pm 0.00005^\circ\text{C}$ for 60 sec.